

Entropy production in relativistic binary mixtures

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Abstract

In this paper we calculate the entropy production of a relativistic binary mixture of inert dilute gases using kinetic theory. For this purpose we use the covariant form of Boltzmann's equation which, when suitably transformed, yields a formal expression for such quantity. Its physical meaning is extracted when the distribution function is expanded in the gradients using the well-known Chapman-Enskog method. Retaining the terms to first order, consistently with Linear Irreversible Thermodynamics we show that indeed, the entropy production can be expressed as a bilinear form of products between the fluxes and their corresponding forces. The implications of this result are thoroughly discussed.

I. INTRODUCTION

In a recent paper [1] we have studied two important thermodynamic aspects of a relativistic binary mixture of inert dilute gases using the principles of kinetic theory. The first one concerns the so called cross effects, in this case when local thermal equilibrium is assumed, they are the well known Dufour and Soret effects [2]. The second and most relevant one, concerns with the validity of the Onsager Reciprocity Relations (ORR). As we showed in that paper they hold true in two representations, or choices, of fluxes and forces. In the first representation, which is referred to it in the literature [3, 4] the heat flux is coupled to a modified Fourier-like force involving both, temperature and pressure gradients. In such representation however, the Dufour and Soret effects do not appear in their canonical form. The second representation is rather singular. Introducing the concept of a “volumetric flow” which arises from the relativistic non-invariance of the volume elements in the fluid and whose force turns out to be the pressure gradient, the ORR are shown to hold true and the canonical form of such effects is recovered. Further, this representation is strictly valid only in the relativistic case.

As it is well-known in Linear Irreversible Thermodynamics (LIT) [2] the appropriate choice of forces and fluxes is strongly suggested by the entropy balance equation which in kinetic theory arises by simply multiplying Boltzmann’s equation by the logarithm of the single particle distribution function and averaging over all the velocities of the particles. This procedure allows one to identify the entropy production, usually denoted by σ as a bilinear form of products between forces and fluxes. Symbolically, if X_i is the force associated with a flux J_i ,

$$\sigma = \sum_i X_i \odot J_i \quad (\text{I.1})$$

where, for an isotropic system, \odot denotes full contraction of the two tensors, necessarily of the same rank.

The full derivation of Eq. (I.1) for a relativistic binary mixture of inert, diluted gases is the main objective of this paper. The outcome of this derivation should provide full support for the force-flux representations used in [1]. Since the whole scheme of both papers is restricted to the tenets of LIT we will only need to carry out the calculation using the well-known Chapman-Enskog expansion to

first order in the gradients. As shown in Ref. [5] this procedure is perfectly valid in a relativistic framework characterized by Minkowski's metric namely, in special relativity.

To facilitate the reading of this paper we use the following conventions. Tensors with space and time components are labeled with greek subscripts: $\alpha, \beta = 1, 2, 3, 4$, where the fourth component refers to time whereas spatial components are labeled with latin subscripts $i, j = 1, 2, 3$. Einstein's sum convention is adopted for both types of subscripts throughout, but not for sums characterizing the species of the mixture. The Minkowski metric has signature $\{+++-\}$, colons and semicolons denote ordinary and covariant derivatives respectively.

The structure of this paper is as follows: In section 2 the basic ideas of relativistic kinetic theory are explained up to a linearized version of the Boltzmann equation consistent with the Chapman-Enskog expansion. The solution to such equation is proposed in section 3 using the representation introduced in Ref. [1]. The general structure of the entropy balance equation and thus the expression for the entropy production σ are also shown in section 3. Section 4 is devoted to establishing the required form of σ within this representation (LIT). Lastly, in section 5 we give some final remarks.

II. METHOD: RELATIVISTIC KINETIC THEORY

The Boltzmann equation [6] for a mixture of two non-reacting dilute species in thermal local equilibrium reads,

$$v_{(i)}^\alpha f_{(i),\alpha} = \sum_j J_{(ij)} \quad (\text{II.1})$$

where the collisional term is given by [4],

$$\sum_j J_{(ij)} = \sum_j \int (f'_{(i)} f'_{(j)} - f_{(i)} f_{(j)}) F_{(ij)} \Sigma_{(ij)} d\Omega_{(ji)} dv_{(j)}^*. \quad (\text{II.2})$$

Here, $F_{(ij)}$, $\Sigma_{(ij)}$ and $d\Omega_{(ji)}$ denote the invariant flux, the invariant differential elastic cross-section and the element of solid angle that characterizes a binary collision between particles of the same species as well as those between different species. The differential $dv_{(i)}^*$ stands for $\frac{d^3 v_{(i)}}{v_{(i)}^4}$, which is also an invariant. The cross-section $\Sigma_{(ij)}$ has special symmetries [7–9] that guarantee the existence

of inverse collisions such that the principle of microscopic reversibility and therefore an H theorem are satisfied.

It is important to notice that the molecular velocity $v_{(i)}^\mu$ is measured by an observer in an arbitrary frame, in which the four-velocity of the fluid is represented by U^μ . This frame is called the laboratory frame.

From Eq. (II.1) one can obtain the balance equations by multiplying it by the collisional invariants namely, the rest mass $m_{(i)}$, the four-momentum $m_{(i)}v_{(i)}^\mu$ and then integrating over the velocities $dv_{(i)}^*$. The complete set of equations can be found in Ref. [10]. In this work we only need them at lowest order in the gradients. This is accomplished through the use of the Chapman-Enskog [5, 11] method of solution to Eq. (II.1). The particle number density conservation for each species reads as,

$$n_{(i)}U_{;\alpha}^\alpha + U^\alpha n_{(i),\alpha} = 0, \quad (\text{II.3})$$

the momentum balance as

$$\tilde{\rho}U^\mu U_{;\mu}^\beta + h^{\beta\nu}p_{,\nu} = 0 \quad (\text{II.4})$$

and finally, the energy conservation as

$$nU^\nu e_{,\nu} = -pU_{;\mu}^\mu. \quad (\text{II.5})$$

Here,

$$n = n_{(i)} + n_{(j)} \quad (\text{II.6})$$

is the total particle density, and

$$\tilde{\rho} = \sum_i m_{(i)}n_{(i)}G(z_{(i)}) = \tilde{\rho}_{(1)} + \tilde{\rho}_{(2)}, \quad (\text{II.7})$$

with

$$G(z_{(i)}) = \frac{\mathcal{K}_3\left(\frac{1}{z_{(i)}}\right)}{\mathcal{K}_2\left(\frac{1}{z_{(i)}}\right)}, \quad (\text{II.8})$$

and $h^{\beta\alpha} = g^{\beta\alpha} + c^{-2}U^\beta U^\alpha$ is a projector in the direction orthogonal to U^α . Here $\mathcal{K}_n\left(\frac{1}{z_{(i)}}\right)$ is the modified Bessel function of the second kind for the integer n .

We now expand Eq. (II.1) using the well-known Chapman-Enskog series [5, 11] up to first order in the gradients namely,

$$f_{(i)} = f_{(i)}^{(0)} (1 + \phi_{(i)}), \quad (\text{II.9})$$

where $f_{(i)}^{(0)}$ is the local equilibrium distribution namely, Jüttner's distribution [12, 13] which is given by,

$$f_{(i)}^{(0)} = \frac{n_{(i)}}{4\pi c^3 z_{(i)} \mathcal{K}_2\left(\frac{1}{z_{(i)}}\right)} \exp\left(\frac{U^\beta v_{(i)\beta}}{z_{(i)} c^2}\right), \quad (\text{II.10})$$

with $z_{(i)} = \frac{k_B T}{m_{(i)} c^2}$. Moreover, we must now introduce the functional hypothesis namely $f_{(i)}(x^\alpha, v_{(i)}^\alpha | n_{(i)}, U^\alpha, T)$, implying that the representation chosen is defined by the locally conserved variables $n_{(i)}$, U^β and T . We remind the reader that this assumption constitutes one possibility of extracting from the manifold of the possible solutions of the Boltzmann equations those which are consistent with the hydrodynamics of the fluid Ref. [14] (also known in the literature as Hilbert's paradox).

From now on, we will develop all the calculations in the local co-moving frame, where the spatial components of the hydrodynamical four-velocity vanish, i.e. $U^m = 0$. This frame has the advantage that allows us to isolate the purely kinetic effects of the motion of the particles from the convective effects [15–17]. Then we can transform all the quantities measured in such frame to an arbitrary one with four-velocity U^β through a Lorentz transformation. Indeed, denoting by \mathcal{L}_ν^μ the Lorentz transformation, the molecular four-velocity in a moving frame reads as,

$$v_{(i)}^\mu = \mathcal{L}_\nu^\mu K_{(i)}^\nu. \quad (\text{II.11})$$

Here $K_{(i)}^\nu$ is the four-velocity in the local co-moving frame. In the classical framework it is precisely the definition of the well known peculiar or thermal velocity [11].

The definition of the dissipative mass flux, heat flux and viscous tensor are established when we obtain the complete set of transport equations (see Ref. [10]) in the local co-moving frame. They are given by,

$$J_{(i)}^m = m_{(i)} \int K_{(i)}^m f_{(i)} dK_{(i)}^*, \quad (\text{II.12})$$

$$q_{(i)}^m = m_{(i)} c^2 \int \gamma_{k_{(i)}} K_{(i)}^m f_{(i)} dK_{(i)}^* \quad (\text{II.13})$$

and

$$\pi_{(i)}^{mn} = m_{(i)} \int K_{(i)}^m K_{(i)}^n f_{(i)} dK_{(i)}^* \quad (\text{II.14})$$

respectively. Here $\gamma_{k_{(i)}} = \left(1 - \frac{k_{(i)}^2}{c^2}\right)^{-1/2}$.

After some algebra, the expansion of the Boltzmann equation (II.1) with the help of Eqs. (II.9), (II.3), (II.4), (II.5) leads to the following equation,

$$\begin{aligned} K_{(i)}^m \left\{ -\gamma_{k_{(i)}} \frac{1}{z_{(i)} c^2 \bar{\rho}} p_{,m} + (\ln n_{(i)})_{,m} + \left[1 + \frac{1}{z_{(i)}} \left(\gamma_{k_{(i)}} - G(z_{(i)}) \right) \right] (\ln T)_{,m} \right\} \\ + \frac{1}{z_{(i)} c^2} \left(K_{(i)}^m \overset{\circ}{K}_{(i)n} \right) U_{;m}^n + \tau_{(i)} U_{;m}^m \\ = [C(\phi_{(i)}) + C(\phi_{(i)} + \phi_{(j)})], \end{aligned} \quad (\text{II.15})$$

where,

$$K_{(i)}^m K_{(i)n} = \left(K_{(i)}^m \overset{\circ}{K}_{(i)n} \right) + \tau_{(i)} \delta_n^m. \quad (\text{II.16})$$

Here $\tau_{(i)}$ corresponds to the trace of the tensor $K_{(i)}^m K_{(i)n}$ and it is related to the dynamic pressure, while $\left(K_{(i)}^m \overset{\circ}{K}_{(i)n} \right)$ denotes the symmetric traceless part. The collisional linearized kernels are

$$[C(\phi_{(i)}) + C(\phi_{(i)} + \phi_{(j)})] = \sum_i \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} (\phi_{(i)}' + \phi_{(j)}' - \phi_{(i)} - \phi_{(j)}) F_{(ij)} \Sigma_{(ij)} d\Omega_{(ji)} dK_{(j)}^*. \quad (\text{II.17})$$

The form of Eq. (II.15) is crucial in order to identify the thermodynamical forces. As we have said, the subtle decision of how it can be rearranged has been studied in a previous work [1] by addressing the necessity of complying with the ORR. This is accomplished through the introduction of a pseudo-flux which arises strictly from relativistic considerations and is directly related to the term containing the pressure gradient ($\sim p_{,m}$, recall that $p_{(i)} = n_{(i)} k_B T$). Such a flux, we insist appears only in the relativistic kinetic theory with $p_{,m}$ acting as its direct force and can be explained by taking the averages of microscopic Lorentz deformations of spatial cells and thus we may refer to it as a “volume flux”. This idea has never been dealt within the literature before [3, 18] and has the advantage of allowing a clear definition of both the Soret and Dufour effects in a relativistic framework.

III. LINEAR THEORY

By following the arguments that we have discussed in the previous section it is possible to rearrange the linearized Boltzmann equation (II.15) as follows[1],

$$\begin{aligned} K_{(i)}^m \left\{ d_m + \frac{1}{z_{(i)}} \left(\gamma_{k_{(i)}} - G(z_{(i)}) \right) \frac{T_{,m}}{T} - \left(\gamma_{k_{(i)}} - G(z_{(i)}) \right) V_{(i)m} \right\} \\ + \frac{1}{z_{(i)} c^2} \left(K_{(i)}^m K_{(i)n} \right) U_{;m}^n + \tau_{(i)} U_{;m}^m \\ = \left[C(\phi_{(i)}) + C(\phi_{(i)} + \phi_{(j)}) \right], \end{aligned} \quad (\text{III.1})$$

for species i . Recall that there is a similar equation for species j . Here

$$V_m \equiv V_{(i)m} = \frac{m_{(i)}}{m_{(j)}} V_{(j)m} = \frac{n_{(i)} m_{(i)}}{\tilde{\rho}} \frac{p_{,m}}{p_{(i)}} \quad (\text{III.2})$$

represents a new relativistic thermodynamic pseudo-force $V_{(i)m}$ related with Lorentz contractions of the mean free path of the particles. In Ref. [1] it has been clearly shown that the corresponding transport coefficients satisfy the symmetries required by the Onsager reciprocity relations. Notice also that here we have a relativistic generalization of the diffusive force

$$d_m = d_{m(i)} = -d_{m(j)} = n_{(j)} \left(\frac{m_{(j)} G(z_{(j)}) - m_{(i)} G(z_{(i)})}{\tilde{\rho}} \right) \frac{p_{,m}}{p} + \frac{n}{n_{(i)}} (n_{i0})_{,m}, \quad (\text{III.3})$$

with $n_{i0} = \frac{n_{(i)}}{n}$. In the non-relativistic limit one recovers the usual expression [2, 19],

$$d_m \rightarrow \frac{n_{(j)}}{\rho p} (m_{(j)} - m_{(i)}) \nabla p + \frac{n}{n_{(i)}} \nabla n_{i0}. \quad (\text{III.4})$$

Now we proceed to the solution of Eq. (III.1) [5, 24],

$$\phi_{(i)} = -K_{(i)}^m A_{(i)} \frac{T_{,m}}{T} - \sum_j K_{(j)}^m B_{(j)}^{(i)} V_m - \sum_j K_{(j)}^m D_{(j)}^{(i)} d_m - L_{(i)n}^m U_{;m}^n. \quad (\text{III.5})$$

Notice that when Eq. (III.5) is substituted into Eqs. (II.12) and (II.13) we obtain the heat and mass fluxes in which the Soret and Dufour effects are clearly identified. Indeed, de Soret coefficient is given by,

$$\sum_{(i)} \int f_{(i)}^{(0)} K_{(i)}^n K_{n(i)} A_{(i)} dK_{(i)}^* \quad (\text{III.6})$$

and the Dufour by,

$$\sum_{(i),(j)} \int f_{(i)}^{(0)} \frac{1}{z_{(i)}} \left(\gamma_{k_{(i)}} - G(z_{(i)}) \right) K_{(i)}^n K_{n(i)} D_{(j)}^{(i)} dK_{(i)}^* \quad (\text{III.7})$$

which have been shown to be symmetric in Ref. [1].

As it has been thoroughly discussed in Ref. [1], the pseudo force V_m corresponds to a relative flux directly associated with Lorentz deformations in the microscopic geometrical aspects of the system. Such a flux which we have called a “volume flux” is a novel quantity. Although in non-relativistic fluid dynamics the concept of a volume flow dates back to Burnett [20], it has been recently revived by Brenner [21–23], but in our previous work [1] it arises strictly from relativistic considerations. In this paper, such flux which we will denote as J_V^m is precisely the conjugate of the pseudo force V_m . Also it is important to underline the fact that both J_V^m and V_m vanish in the non-relativistic limit.

Now we will use Eq. (III.5) to find the entropy production which, in analogy with the non-relativistic case is identified from a balance equation of the form

$$\frac{\partial}{\partial t} (ns) + \nabla \cdot (\vec{J}_s) = \sigma. \quad (\text{III.8})$$

To accomplish this task, we consider the entropy four-flux in an arbitrary frame

$$S^\mu \equiv -k_B \sum_{(i)} \int v_{(i)}^\mu f_{(i)} (\ln f_{(i)} - 1) dv_{(i)}^*, \quad (\text{III.9})$$

which we decompose as [4],

$$S^\mu = aU^\mu + \phi^\mu, \quad (\text{III.10})$$

where ϕ^μ is a four vector orthogonal to U^μ . The invariant a can be thus expressed as

$$a = -\frac{S^\mu U_\mu}{c^2} \quad (\text{III.11})$$

or

$$a = \frac{k_B}{c^2} \sum_{(i)} U_\mu \int v_{(i)}^\mu f_{(i)} (\ln f_{(i)} - 1) dv_{(i)}^*. \quad (\text{III.12})$$

Recalling the properties of invariants, we notice that,

$$U^\mu v_{(i)\mu} = -\gamma_{k_{(i)}} c^2. \quad (\text{III.13})$$

Moreover, using that $dv_{(i)}^* = d^3v_{(i)}/\gamma_{v_{(i)}} = d^3K_{(i)}/\gamma_{k_{(i)}}$, we have that

$$a = -k_B \sum_{(i)} \int f_{(i)} (\ln f_{(i)} - 1) d^3K_{(i)}, \quad (\text{III.14})$$

which is readily identified with the local entropy density s for the mixture. In appendix A, it is shown that the entropy four-flux defined in Eq. (III.9) satisfies a balance equation of the form

$$S_{;\mu}^\mu = \sigma \quad (\text{III.15})$$

where σ is the entropy production given by

$$\sigma = -k_B \sum_{(i),(j)} \int J(f_{(i)} f_{(j)}) \ln f_{(i)} dv_{(i)}^*. \quad (\text{III.16})$$

In the next section we will provide thermodynamical content to Eq. (III.16). Indeed, what we will show is that σ may be related to Eq. (I.1) only when $f_{(i)}$ is written in terms of the state variables.

IV. DERIVATION OF σ

In order to carry out the program outlined in the previous section, we start with the property that the Boltzmann equation is a relativistic invariant. We next choose the co-moving frame for performing the calculations which will be carried out only to first order in gradients. For this purpose we analyze Eq. (III.16) expanded with the help of Eq. (II.9). Thus,

$$\sigma = -k_B \sum_{(i),(j)} \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} (\phi_{(i)}' + \phi_{(j)}' - \phi_{(i)} - \phi_{(j)}) \ln \left[f_{(i)}^{(0)} (1 + \phi_{(i)}) \right] F_{(ij)} \Sigma_{(ij)} d\Omega_{(ji)} dK_{(j)}^* dK_{(i)}^*. \quad (\text{IV.1})$$

Now we expand $\ln \left[f_{(i)}^{(0)} (1 + \phi_{(i)}) \right]$ in a neighborhood of $\phi_{(i)} \ll 1$,

$$\ln \left[f_{(i)}^{(0)} (1 + \phi_{(i)}) \right] \simeq \ln f_{(i)}^{(0)} + \phi_{(i)} + O(\phi_{(i)}^2), \quad (\text{IV.2})$$

so we have,

$$\sigma = -k_B \sum_{(i),(j)} \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} (\phi_{(i)}' + \phi_{(j)}' - \phi_{(i)} - \phi_{(j)}) \left(\ln f_{(i)}^{(0)} + \phi_{(i)} \right) F_{(ij)} \Sigma_{(ij)} d\Omega_{(ji)} dK_{(j)}^* dK_{(i)}^*. \quad (\text{IV.3})$$

Noticing that $\ln f_{(i)}^{(0)}$ is a combination of all collisional invariants, all integrals associated to it vanish. Whence

$$\sigma = -k_B \sum_{(i),(j)} \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} (\phi_{(i)}' + \phi_{(j)}' - \phi_{(i)} - \phi_{(j)}) \phi_{(i)} F_{(ij)} \Sigma_{(ij)} d\Omega_{(ji)} dK_{(j)}^* dK_{(i)}^*, \quad (\text{IV.4})$$

which, with the help of Eq. (II.17), is easily written as

$$\sigma = -k_B \sum_{(i),(j)} \int [C(\phi_{(i)}) + C(\phi_{(i)} + \phi_{(j)})] \phi_{(i)} dK_{(i)}^*. \quad (\text{IV.5})$$

Finally, by using Eq. (II.15) we get,

$$\begin{aligned} \sigma = & -k_B \sum_{(i)} \int f_{(i)}^{(0)} \left[K_{(i)}^m \left\{ d_m + \frac{1}{z_{(i)}} (\gamma_{k_{(i)}} - G(z_{(i)})) \frac{T_{,m}}{T} - (\gamma_{k_{(i)}} - G(z_{(i)})) V_{(i)m} \right\} \right. \\ & \left. + \frac{1}{z_{(i)} c^2} \left(K_{(i)}^m K_{(i)n} \right) U_{;m}^n + \tau_{(i)} U_{;m}^m \right] \phi_{(i)} dK_{(i)}^*. \end{aligned} \quad (\text{IV.6})$$

Where $\phi_{(i)}$ is given by Eq. (III.5).

Carrying out the ensuing algebra (see appendix B) one arrives at,

$$\frac{\sigma}{k_B} = -J^{m*} [d_m] - q^{m*} \left[\frac{T_{,m}}{T} \right] - J_V^m V_m - \frac{1}{k_B T} \pi_n^m U_{;m}^n - \tau U_{;m}^m. \quad (\text{IV.7})$$

In Eq. (IV.7), we identify the vector fluxes namely, the diffusive mass flux as,

$$J^{m*} = \sum_{(i)} \frac{J_{(i)}^m}{m_{(i)}} = \sum_{(i)} \int K_{(i)}^m f_{(i)}^{(0)} \phi_{(i)} dK_{(i)}^*, \quad (\text{IV.8})$$

the energy transport,

$$q^{m*} = \frac{1}{k_B T} \sum_{(i)} \left(q_{(i)}^m - h_{(i)} \frac{J_{(i)}^m}{m_{(i)}} \right) \quad (\text{IV.9})$$

where

$$h_{(i)} = \frac{k_B T}{z_{(i)}} G(z_{(i)}) \quad (\text{IV.10})$$

is the specific enthalpy, and the new ingredient, the “volume flux”,

$$J_V^m = \sum_{(i)} \left(J_{v(i)}^m - \frac{h_{E(i)}}{m_{(i)} c^2} \frac{J_{(i)}^m}{m_{(i)}} \right), \quad (\text{IV.11})$$

where $h_{E(i)} = \frac{\bar{\rho}_{(i)} c^2}{n_{(i)}}$ depends of the enthalpy through Eq. (II.7). The volume flux $J_{v(i)}^m$ is defined trough a corresponding balance equation [1].

On the other hand we have the tensor fluxes,

$$\pi_n^m = \sum_{(i)} \pi_{(i)n}^m = \sum_{(i)} \int (K_{(i)}^m K_{(i)n}) f_{(i)}^{(0)} \phi_{(i)} dK_{(i)}^* \quad (\text{IV.12})$$

$$\tau = \sum_{(i)} \tau_{(i)} = \sum_{(i)} \int K_{(i)}^n K_{(i)n} f_{(i)}^{(0)} \phi_{(i)} dK_{(i)}^*. \quad (\text{IV.13})$$

It is important to notice that the structure of these fluxes is the necessary required to obtain the canonical form for the entropy production namely,

$$\sigma = \sum_i J_i \odot X_i, \quad (\text{IV.14})$$

where \odot is the contraction to a scalar of fluxes with their corresponding forces in accordance with Curie's theorem. Equation (IV.14) is in complete accordance with the Linear Irreversible Thermodynamics. Notice that a completely equivalent argument can be given for the other representation but since it has been carried out in the literature [4] we omit it.

V. FINAL REMARKS

In this work we have obtained the entropy production for a relativistic binary mixture to first order in the gradients using the completely new idea of “volume flux” Ref. [1]. In such paper, the “volume flux” is produced with the next simple idea: Imagine the motion of a single particle, then construct an imaginary volume around it with radius a , where a is the mean free path. Such a volume would remain spherical in the non-relativistic scheme, but because of the Lorentz contraction it would be deformed in the relativistic framework. When we average these microscopic deformations per particle we obtain the “volume flux”. Indeed, when we multiply Boltzmann's equation by the microscopic change in the volume $a\gamma_{k(i)}$, and then integrate over the velocities $dK_{(i)}^*$ we find,

$$\left(\int \gamma_{k(i)} K_{(i)}^\alpha f_{(i)} dK_{(i)}^* \right)_{,\alpha} = \int \gamma_{k(i)} (J_{(ii)} + J_{(ij)}) dK_{(i)}^* \quad (\text{V.1})$$

$$= \pi_{vol},$$

which is a balance equation for the change in the volume in the gas, and defines,

$$J_{v(i)}^\alpha = \int \gamma_{k(i)} K_{(i)}^\alpha f_{(i)} dK_{(i)}^*. \quad (\text{V.2})$$

Notice that in the non-relativistic limit, the right hand side vanishes, implying that there is no such change in volume. On the other hand, in the one-component limit J_v^α turns out to be a multiple of the heat flux q^α , indeed $\frac{q^\alpha}{k_B T} = \frac{1}{z} J_v^\alpha$.

The corresponding expression for the “volume flux” is valid only in the co-moving frame. This however has no restriction since to obtain the same quantity in an arbitrary frame one may simply resort to the well-known Lorenz transformations.

The form of the fluxes here obtained in Eqs. (IV.8) (IV.9) (IV.11) (IV.12) and (IV.13) is in accordance with LIT and supports the definitions obtained in a previous work [1]. Notice that, in the non-relativistic limit, the term corresponding to the volume flux J_V^m in Eq. (IV.7) or (V.21) vanishes because

$$\gamma_{k(i)} - G(z(i)) \rightarrow 0, \quad (\text{V.3})$$

so we recover the classical expression for the entropy production [11].

The generalization of the Soret and Dufour effects found in a previous work Ref. [1] are now formally sustained by Eq. (IV.7). Their corresponding coefficients are easily found when Eq. (IV.8) and (IV.9) are expanded using the Chapman-Enskog method. Additionally we have two more new coefficients related with V^m whose physical meaning remains to be studied.

We would like to emphasize at this stage that the entropy production as defined here and in general, in LIT is unfortunate [25]. Logically speaking it has no meaning since entropy as any other state variable such as energy, pressure, volume, etc, can not be “produced”. It is a pity that the original concept of uncompensated heat defined as $T\sigma$ as originally introduced by Clausius Ref. [26] has not been kept. Uncompensated heat is the energy that arises in any thermodynamic process due to dissipative effects, and further what one can measure in the laboratory is heat, not entropy.

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Appendix A

Let

$$S^\mu \equiv -k_B \sum_{(i)} \int v_{(i)}^\mu f_{(i)} (\ln f_{(i)} - 1) dv_{(i)}^* \quad (\text{V.4})$$

be the entropy four-flux. Then,

$$S_{;\mu}^\mu = \sigma \quad (\text{V.5})$$

where

$$\sigma = -k_B \sum_{(i),(j)} \int J(f_{(i)} f_{(j)}) \ln f_{(i)} dv_{(i)}^* \geq 0 \quad (\text{V.6})$$

and $J(f_{(i)} f_{(j)})$ is defined in Eq. (II.2).

Let us start with the four-divergence of Eq. (V.4),

$$\begin{aligned} S_{;\mu}^\mu &= \left(-k_B \sum_{(i)} \int v_{(i)}^\mu f_{(i)} (\ln f_{(i)} - 1) dv_{(i)}^* \right)_{;\mu} \\ &= -k_B \sum_{(i)} \int \left[v_{(i)}^\mu f_{(i)} (\ln f_{(i)} - 1) \right]_{;\mu} dv_{(i)}^* \\ &= -k_B \sum_{(i)} \int \left[\left(v_{(i)}^\mu f_{(i)} \ln f_{(i)} \right)_{;\mu} - \left(v_{(i)}^\mu f_{(i)} \right)_{;\mu} \right] dv_{(i)}^* \\ &= -k_B \sum_{(i)} \int \left[v_{(i);\mu}^\mu f_{(i)} (\ln f_{(i)} - 1) + v_{(i)}^\mu f_{(i);\mu} \ln f_{(i)} \right] dv_{(i)}^*. \end{aligned} \quad (\text{V.7})$$

Now we substitute the Boltzmann Equation (II.1) in the second term of the right hand side, which reads

$$S_{;\mu}^\mu = -k_B \sum_{(i)} \int \left[v_{(i);\mu}^\mu f_{(i)} (\ln f_{(i)} - 1) + \sum_{(j)} J(f_{(i)} f_{(j)}) \ln f_{(i)} \right] dv_{(i)}^*, \quad (\text{V.8})$$

then

$$-k_B \sum_{(i)} \int v_{(i);\mu}^\mu f_{(i)} (\ln f_{(i)} - 1) dv_{(i)}^* = -k_B \sum_{(i),(j)} \int J(f_{(i)} f_{(j)}) \ln f_{(i)} dv_{(i)}^*, \quad (\text{V.9})$$

so the entropy four-flux is given by

$$S^\mu = -k_B \sum_{(i)} \int v_{(i)}^\mu f_{(i)} (\ln f_{(i)} - 1) dv_{(i)}^* \quad (\text{V.10})$$

and the production term,

$$\sigma = -k_B \sum_{(i),(j)} \int J(f_{(i)} f_{(j)}) \ln f_{(i)} dv_{(i)}^*. \quad (\text{V.11})$$

It is important to underline here that the identification of S^4 with the local entropy, S^m with the entropy diffusive flux and σ with the non compensated heat is not complete until the solution $f_{(i)}$ is determined. Indeed, while $f_{(i)}$ remains unknown, none of these quantities can be taken as a function of thermodynamic variables because they do not appear in $f_{(i)}$.

On the other hand,

$$\sigma = -k_B \sum_{(i),(j)} \int J(f_{(i)} f_{(j)}) \ln f_{(i)} dv_{(i)}^* \quad (\text{V.12})$$

$$\sigma = -k_B \sum_{(i),(j)} \int (f'_{(i)} f'_{(j)} - f_{(i)} f_{(j)}) \ln f_{(i)} F_{(ij)} \sigma_{(ij)} d\Omega_{(ji)} dv_{(j)}^* dv_{(i)}^*, \quad (\text{V.13})$$

which, by using the same transformations as those performed in the proof the H theorem it can be written as

$$\sigma = \frac{1}{4} k_B \sum_{(i),(j)} \int (f'_{(i)} f'_{(j)} - f_{(i)} f_{(j)}) \ln \frac{f'_{(i)} f'_{(j)}}{f_{(i)} f_{(j)}} F_{(ij)} \sigma_{(ij)} d\Omega_{(ji)} dv_{(j)}^* dv_{(i)}^*. \quad (\text{V.14})$$

Therefore, with the Klein's inequality,

$$(f'_{(i)} f'_{(j)} - f_{(i)} f_{(j)}) \ln \frac{f'_{(i)} f'_{(j)}}{f_{(i)} f_{(j)}} \geq 0, \quad (\text{V.15})$$

one obtains

$$\sigma \geq 0. \quad (\text{V.16})$$

We recall the reader that Eq. (V.16) is valid for any exact solution of the Boltzmann equation and has no inherent physical meaning until one establishes the form of $f_{(i)}$.

Appendix B

First recall Eq. (IV.6),

$$\sigma = -k_B \sum_{(i)} \int f_{(i)}^{(0)} \left[K_{(i)}^m \left\{ d_m + \frac{1}{z_{(i)}} \left(\gamma_{k_{(i)}} - G(z_{(i)}) \right) \frac{T_m}{T} - \left(\gamma_{k_{(i)}} - G(z_{(i)}) \right) V_{(i)m} \right\} + \frac{1}{z_{(i)} c^2} \left(K_{(i)}^m K_{(i)n} \right) U_{;m}^n + \tau_{(i)} U_{;m}^m \right] \phi_{(i)} dK_{(i)}^*, \quad (\text{V.17})$$

so,

$$\begin{aligned} \frac{\sigma}{-k_B} = & \sum_{(i)} \int K_{(i)}^m \phi_{(i)} d^3 K_{(i)}^* d_m + \sum_{(i)} \int K_{(i)}^m \frac{1}{z_{(i)}} \left(\gamma_{k_{(i)}} - G(z_{(i)}) \right) \phi_{(i)} dK_{(i)}^* \frac{T_{,m}}{T} \\ & - \sum_{(i)} \int K_{(i)}^m \left(\gamma_{k_{(i)}} - G(z_{(i)}) \right) \phi_{(i)} dK_{(i)}^* V_{(i)m} \\ & + \sum_{(i)} \int \frac{1}{z_{(i)} c^2} \left(K_{(i)}^m K_{(i)n} \right) \phi_{(i)} dK_{(i)}^* U_{;m}^n + \sum_{(i)} \int \tau_{(i)} \phi_{(i)} dK_{(i)}^* U_{;m}^m. \end{aligned} \quad (\text{V.18})$$

Here, we identify the bilinear form: fluxes times forces structure. The coefficient of the diffusive force is

$$\frac{J_{(i)}^m}{m_{(i)}} = \int K_{(i)}^m \phi_{(i)} dK_{(i)}^*. \quad (\text{V.19})$$

For the temperature gradient, the coefficient is

$$\begin{aligned} \sum_{(i)} \int K_{(i)}^m \frac{1}{z_{(i)}} \left(\gamma_{k_{(i)}} - G(z_{(i)}) \right) \phi_{(i)} dK_{(i)}^* &= \sum_{(i)} \left[\int K_{(i)}^m \frac{\gamma_{k_{(i)}}}{z_{(i)}} \phi_{(i)} dK_{(i)}^* \right. \\ &\quad \left. - \frac{G(z_{(i)})}{z_{(i)}} \int K_{(i)}^m \phi_{(i)} dK_{(i)}^* \right] \\ &= \frac{1}{k_B T} \left(q^m - h_{(i)} \frac{J_{(i)}^m}{m_{(i)}} \right), \end{aligned} \quad (\text{V.20})$$

where $h_{(i)} = \frac{k_B T}{z_{(i)}} G(z_{(i)})$ is the specific enthalpy per species.

The coefficient of the new force $V_{(i)m}$ is given by

$$\begin{aligned} \sum_{(i)} \int K_{(i)}^m \left(\gamma_{k_{(i)}} - G(z_{(i)}) \right) \phi_{(i)} dK_{(i)}^* &= \sum_{(i)} \left[\int K_{(i)}^m \gamma_{k_{(i)}} \phi_{(i)} dK_{(i)}^* \right. \\ &\quad \left. - G(z_{(i)}) \int K_{(i)}^m \phi_{(i)} dK_{(i)}^* \right] \\ &= \sum_{(i)} \left(J_{v(i)}^m - \frac{h_{E(i)}}{m_{(i)} c^2} \frac{J_{(i)}^m}{m_{(i)}} \right) \end{aligned} \quad (\text{V.21})$$

where $h_{E(i)} = \frac{\tilde{\rho}_{(i)} c^2}{n_{(i)}}$, and J_v is defined in Eq. (V.2).

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